

524 887

Rec PCT/PTC 16 FEB 2005

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
26 February 2004 (26.02.2004)

PCT

(10) International Publication Number
WO 2004/016817 A1

(51) International Patent Classification⁷:
B22F 9/02, 9/04, H01M 4/38, C01B 3/00

C22C 1/04,

(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey
Technology Centre, Blounts Court, Sonning Common,
Reading RG4 9NH (GB).

(21) International Application Number:

PCT/GB2003/003318

(22) International Filing Date: 1 August 2003 (01.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0219112.0

16 August 2002 (16.08.2002) GB

(71) Applicants (for all designated States except US): **JOHN-
SON MATTHEY PUBLIC LIMITED COMPANY**
[GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London
SW1Y 5QB (GB). **INSTITUT FUR FESTKOR-
PER-UND WERKSTOFFFORSCHUNG DRESDEN**
[DE/DE]; e.V., Helmholtzstr.20, 01069 Dresden (DE).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

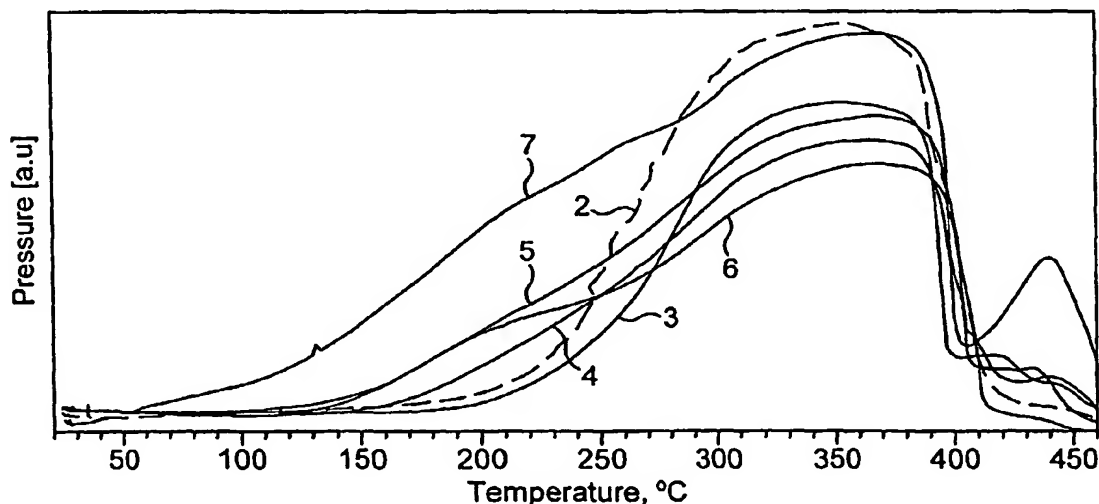
(75) Inventors/Applicants (for US only): **PRATT, Allin,**
Sidney [GB/GB]; 6 The Limes, Crowmarsh Gifford,
Wallingford, Oxfordshire OX10 8HF (GB). **GUT-
FLEISCH, Oliver** [DE/DE]; Eisenacherstr. 19, 01309
Dresden (DE).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: REACTIVE MILLING PROCESS FOR THE MANUFACTURE OF A HYDROGEN STORAGE ALLOY



(57) Abstract: A process for the manufacture of a hydrogen storage material comprises comminuting a source of magnesium under a reducing atmosphere for a time sufficient to produce particles of a required particle size and crystallite size. At least one reducible PGM compound is introduced and substantially reduced during comminution such that it is distributed substantially at the surface of the particles.

WO 2004/016817 A1

REACTIVE MILLING PROCESS FOR THE MANUFACTURE OF A HYDROGEN STORAGE ALLOY

5 This invention relates to a process for the production of hydrogen storage materials and to materials so produced, particularly to a process for the production of hydrogen storage materials based on magnesium and magnesium alloys.

10 Metal hydrides are of great interest as energy storage media. Hydrides of magnesium and magnesium alloys are particularly attractive as they combine potentially high hydrogen storage capacities, 7.6wt% for pure MgH_2 , with low cost and convenient hydride heats of formation. Practical application is however limited due to poor sorption kinetics. For example, conventional hydrogenation of magnesium requires prolonged treatment at temperatures of 300°C and above.

15 Recent studies by Zaluska, *Jn. of Alloys and Compounds*, 288, (1999), p.217-225, have shown that the use of high energy ball milling can improve the hydrogen absorption kinetics of magnesium by promoting a nanocrystalline microstructure. Such processing increases the surface area of the metal so that hydride formation is not limited to the surface regions of the metal and also introduces numerous structural defects which facilitate hydrogen penetration. It is important that the milling process is performed under an inert atmosphere, e.g. argon, to prevent oxidation of the magnesium. Absorption kinetics can be improved such that the time for hydrogenation at 300°C is reduced to a few minutes. Nonetheless, this temperature is still too high for many practical purposes. Other methods of enhancing sorption kinetics have included the use of additives and catalysts. For example, the addition of small amounts of 3d transition metals, such as Ti, V, Mn, Fe or Ni has been reported to allow hydrogen absorption at room temperature and subsequent desorption at 235°C albeit under reduced pressure.

30 WO 9623906 describes the use of high energy ball milling to produce nanocrystalline magnesium and magnesium alloy powders with good hydrogen sorption characteristics. Clusters of platinum group metals, Pd, Pt, Ru, Rh, Ir and Os (referred to hereinafter as PGM) may be attached to the surface of the magnesium particles to catalyse the absorption of hydrogen. The PGM is introduced towards the end of the

milling process. The materials are described as being able to absorb and desorb hydrogen at room temperature and under both low and high pressure however, the specification only contains examples of experiments conducted at 230°C and above. The importance of milling under an inert atmosphere to prevent oxidation of the powders is again stressed. The process has two main drawbacks; firstly the PGM are introduced in metallic (elemental) form which, when finely divided, are extremely pyrophoric, and secondly the processed material still has to be charged with hydrogen before it can be used. This requires extra plant in the form of a hydrogenation vessel, and also equipment to transport the material from the milling apparatus and to the point of use whilst guarding against contamination.

Orimo et al., *Acta mater.* 45, (1997), p.331-341, describe the milling of Mg_2Ni under an atmosphere of hydrogen to produce a nano-structured magnesium-nickel hydride. Care was taken to ensure that no other elements were introduced during processing so avoiding impurity effects on the hydriding and structural properties of the materials.

A desirable aim would be to avoid the use of hazardous, finely divided PGM and produce a hydrogen storage material, charged with hydrogen and ready for use without further processing. This is the aim the present invention sets out to achieve.

In accordance with the present invention, a process for the manufacture of a hydrogen storage material comprises comminuting a source of magnesium under a reducing atmosphere for a time sufficient to produce particles of a required particle size and crystallite size, and introducing at least one reducible PGM compound; wherein the at least one PGM compound is substantially reduced during comminution, and distributed substantially at the surface of the particles.

Preferably, the reducing atmosphere comprises hydrogen. Hydrogen gas may be used either alone or in admixture with an inert gas such as nitrogen or argon. Liquid ammonia may be employed as a source of hydrogen, the ammonia being catalytically

cracked into hydrogen and nitrogen prior to use. The process of cracking liquid ammonia to provide hydrogen is well known and provides advantages in terms of safety and cost.

By using a reducing atmosphere, the present invention has significant advantages over known methods such as that of WO 9623906. Hydrogen is introduced into the lattice of the source of magnesium during comminution. The material obtained is thus already fully hydrogenated, requiring no additional processing before use. It is also thought that the brittleness of the source of magnesium is increased by the presence of lattice hydrogen, leading to more efficient comminution and thus smaller particle and crystallite grain size. A further advantage is the ability to use reducible PGM compounds in place of the metals themselves. As stated above, PGM compounds are less hazardous to use. Also they can, in some cases, be significantly cheaper than the corresponding metals, and are easier to provide in fine particle form.

The source of magnesium may comprise magnesium metal itself, magnesium hydride or an alloy or intermetallic compound, or hydrided alloy or hydrided intermetallic compound of magnesium with one or more other metals. Examples of suitable alloys and intermetallic compounds include binary alloys or intermetallic compounds of magnesium with transition metals such as nickel, iron, or manganese. Any alloy or intermetallic compound may be pre-formed e.g. Mg_2Ni , or alternatively, the alloying elements may be introduced in admixture with magnesium, the comminution process forming the alloy or intermetallic compound via mechanical alloying. Preferably, the source of magnesium comprises magnesium metal, magnesium hydride, a magnesium-nickel alloy or intermetallic compound or a hydrided magnesium-nickel alloy or intermetallic compound. Mixed sources of magnesium may also be used.

The physical form of the source of magnesium is relatively unimportant provided that it can be broken down to the required particle size during comminution. Powders, grains, filings or other bulk forms may all be used, with powders being preferred.

Preferably, the comminution step is performed using a ball mill and more preferably, a high energy ball mill is used. This introduces considerable amounts of

mechanical work into the source of magnesium, reducing both the particle size and the crystallite size. The ratio of the amount of grinding media (balls) to the amount of material to be comminuted can be derived by the skilled man. Suitably, a ratio by weight of media to material of 5 or more is used. Planetary mills, vibratory mills and jet mills are suitable. Alternatively, other known methods of comminution may also be used. Although not required in the process of the present invention, mills which allow for additional heating during comminution may be beneficial in some circumstances.

Preferably, the at least one reducible PGM compound is introduced towards the end of the comminution step. This ensures that the PGM compound, and thus its reduced product, remains on or near the surface of the particles. If the PGM compound is introduced too early in the process, there may be sufficient time for diffusion into the bulk of the source of magnesium, which compromises the catalytic effect of the PGM and hence the hydrogen storage ability of the material. The exact stage at which the PGM compound is introduced will differ depending on factors such as the severity of the comminution process and the initial physical form of the source of magnesium. Typically however, when high energy ball milling is used, the PGM compound may be introduced during the final hour of comminution.

Preferably, the source of the at least one reducible PGM compound comprises an oxide, a hydrated oxide, a halide or other salt, or any mixture thereof. Particularly preferred are oxides and hydrated oxides of palladium, e.g. PdO and PdO.H₂O, and oxides of ruthenium, e.g. RuO₂. Included are species such as ruthenium black and palladium black. Such compounds are readily reduced to the corresponding metals during comminution under hydrogen. Palladium tends to form a thin, discontinuous coating on the particles whereas ruthenium tends to form isolated clusters attached to the particles.

Suitably, the particles have an average particle size of less than 100µm, more suitably less than 20µm, and preferably less than 5µm, for example 1µm.

It is important that the particles also have a small crystallite size. Preferably, the particles have an average crystallite size of less than 100nm, more preferably less than 50nm, for example 30nm.

5 The invention will now be described by way of example only and with reference to the following drawings in which:

Figure 1 shows a graph of the desorption of hydrogen from an uncatalysed sample of nano-crystalline MgH_2 and from a sample of nano-crystalline MgH_2 co-milled
10 with $\text{PdO.H}_2\text{O}$ for 80 hours and not according to the present invention;

Figure 2 shows a graph of the desorption of hydrogen from an uncatalysed sample of nano-crystalline MgH_2 and from samples of nano-crystalline MgH_2 co-milled with ruthenium black for the final 10 hours, 2 hours, 1 hour, 30 minutes and 15 minutes
15 of milling time according to the present invention;

Figure 3 shows a graph of the desorption of hydrogen from an uncatalysed sample of Mg_2Ni and from a sample of Mg_2Ni co-milled with $\text{PdO.H}_2\text{O}$ for the final hour of milling time according to the present invention; and,
20

Figure 4 shows a graph of the desorption of hydrogen from an uncatalysed sample of Mg_2Ni and from samples of Mg_2Ni co-milled with ruthenium black for the final 10 hours, 2 hours, 1 hour, 30 minutes and 15 minutes of milling time according to the present invention.
25

EXAMPLE 1

Preparation of micro-crystalline MgH_2

Magnesium powder of mesh size $45\mu\text{m}$ and purity 99.8% was loaded into a
30 PARR-reactor. The powder was heated to 400°C under a hydrogen pressure of 60 bar for 3 hours.

EXAMPLE 2**Hydrogen desorption measurements**

All samples prepared as described below were subjected to hydrogen desorption measurements using the following procedure. The samples (approx. 100mg) were placed in a dynamic vacuum system and heated at a rate of 10°C/min. All samples were handled in a glove box under an atmosphere of purified argon to prevent contamination. Results are shown in Figs. 1 - 4.

Comparative Example 1

A P6 planetary ball mill was charged with MgH₂ powder as prepared in example 1. The ratio of grinding balls to powder was 13:1 by weight. The powder was then milled under hydrogen (99.9% pure) at a pressure of 7 bar for 80 hours.

Comparative Example 2

Comparative Example 1 was repeated except that the mill was charged with Mg₂Ni powder (<250µm mesh size) instead of MgH₂.

Comparative Example 3

A P6 planetary ball mill was charged with MgH₂ powder as prepared in example 1 and 0.5wt% of PdO.H₂O was added. The ratio of grinding balls to powder was 13:1 by weight. The powder and metal oxide was then co-milled under hydrogen (99.9% pure) at a pressure of 7 bar for 80 hours.

As shown in Fig. 1, there was little difference between the temperature of hydrogen desorption for this sample 1 and that measured for the uncatalysed sample 2 as prepared in Comparative Example 1. This behaviour is attributed to the diffusion of the Pd species into the bulk of the MgH₂ powder which compromises the catalytic activity of the material.

EXAMPLE 4

A P6 planetary ball mill was charged with MgH_2 powder as prepared in example 1. The ratio of grinding balls to powder was 13:1 by weight. The powder was then milled
5 under hydrogen (99.9% pure) at a pressure of 7 bar for 80 hours. In separate experiments, 1wt% of ruthenium black was added for the final 10 hours, 2 hours, 1 hour, 30 minutes and 15 minutes of milling.

As shown in Fig. 2, desorption of hydrogen from the sample co-milled with
10 ruthenium black for the final 10 hours of milling 3 began at substantially the same temperature as that measured for the uncatalysed sample 2 as prepared in Comparative Example 1. A small reduction in the hydrogen desorption temperature was observed for the sample co-milled for the final 2 hours 4. The samples co-milled for the final hour 5 and the final 15 minutes 6 showed a further reduction in the desorption temperature.
15 The optimum co-milling time for this series of experiments was found to be 30 minutes. This sample 7 reduced the onset of desorption to a temperature below 100°C which was in excess of 100°C lower than that found for the uncatalysed sample 2.

20

EXAMPLE 5

A P6 planetary ball mill was charged with Mg_2Ni powder ($<250\mu\text{m}$ mesh size). The ratio of grinding balls to powder was 13:1 by weight. The powder was then milled
25 under hydrogen (99.9% pure) at a pressure of 7 bar for 80 hours. 0.5wt% of $\text{PdO}\cdot\text{H}_2\text{O}$ was added for the final hour of milling.

As shown in Fig. 3, the onset of hydrogen desorption for this sample 8 was approximately 100°C , which was in excess of 50°C lower than that observed for the
30 uncatalysed sample 9 as prepared in Comparative Example 2.

EXAMPLE 6

Example 4 was repeated except that the mill was charged with Mg_2Ni powder (<250 μm mesh size) instead of MgH_2 . Additions of ruthenium black were again performed for the final 10 hours, 2 hours, 1 hour, 30 minutes and 15 minutes of milling in separate experiments.

As shown in Fig. 4, desorption of hydrogen from the sample co-milled with ruthenium black for the final 10 hours of milling 10 was slightly retarded compared to that measured for the uncatalysed sample 9 as prepared in Comparative Example 2. A small reduction in the hydrogen desorption temperature was observed for the sample co-milled for the final 2 hours 11. The samples co-milled for the final hour 12 and the final 30 minutes 13 showed a further reduction in the desorption temperature. A still further reduction was observed for the sample co-milled for the final 15 minutes 14. This sample reduced the onset of desorption to a temperature below 100°C which was in excess of 50°C lower than that found for the uncatalysed sample 9.

CLAIMS

1. A process for the manufacture of a hydrogen storage material, the process
5 comprising comminuting a source of magnesium under a reducing atmosphere for a time
sufficient to produce particles of a required particle size and crystallite size, and
introducing at least one reducible PGM compound; wherein the at least one PGM
compound is substantially reduced during comminution, and distributed substantially at
the surface of the particles.
- 10 2. A process according to claim 1, wherein the reducing atmosphere comprises
hydrogen.
3. A process according to claim 1 or claim 2, wherein the source of magnesium
15 comprises magnesium metal, magnesium hydride or an alloy or intermetallic compound,
or hydrided alloy or hydrided intermetallic compound of magnesium with one or more
other metals.
4. A process according to any preceding claim, wherein comminution is carried out
20 using a ball mill.
5. A process according to any preceding claim, wherein the at least one reducible
PGM compound is introduced towards the end of the comminution step.
- 25 6. A process according to any preceding claim, wherein the at least one reducible
PGM compound comprises an oxide, a hydrated oxide, a halide or other salt, or any
mixture thereof.
7. A process according to claim 6, wherein the at least one reducible PGM
30 compound comprises PdO, PdO.H₂O, palladium black, ruthenium black or RuO₂.

8. A process according to any preceding claim, wherein the particles have an average particle size of less than 100 μ m.

5 9. A process according to any preceding claim, wherein the particles have an average crystallite size of less than 100nm.

10. A hydrogen storage material prepared by a process according to any preceding claim.

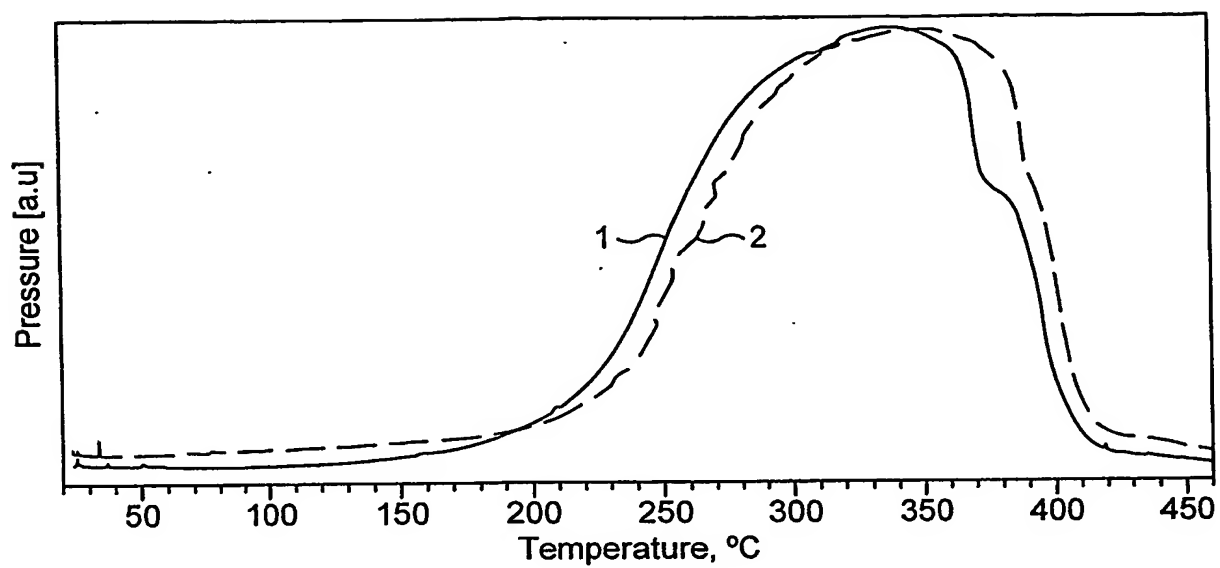


FIG. 1

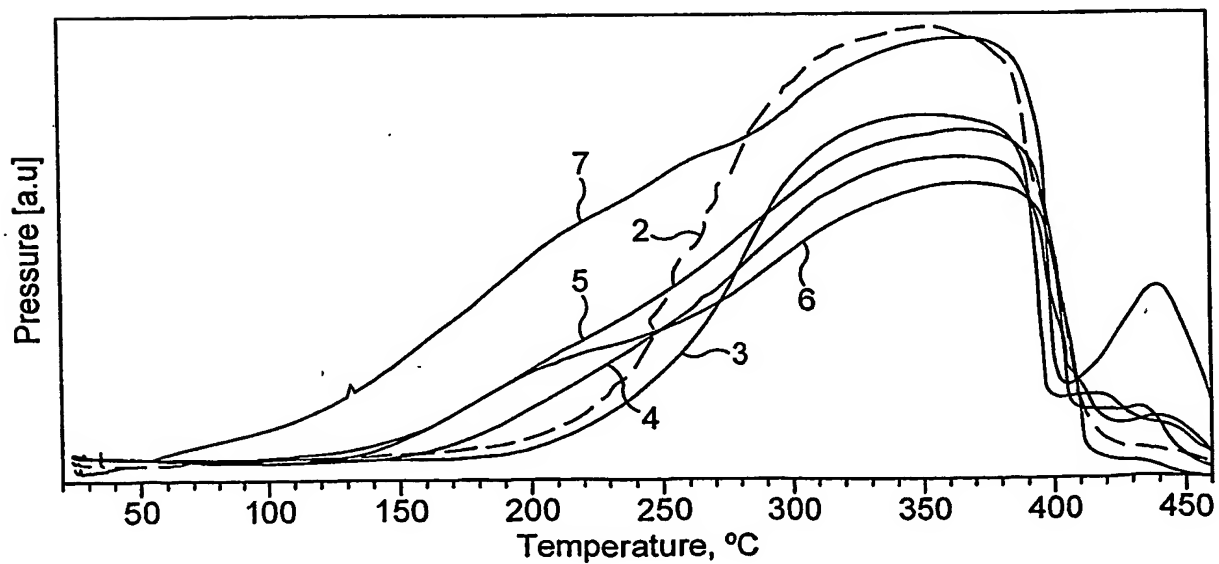


FIG. 2

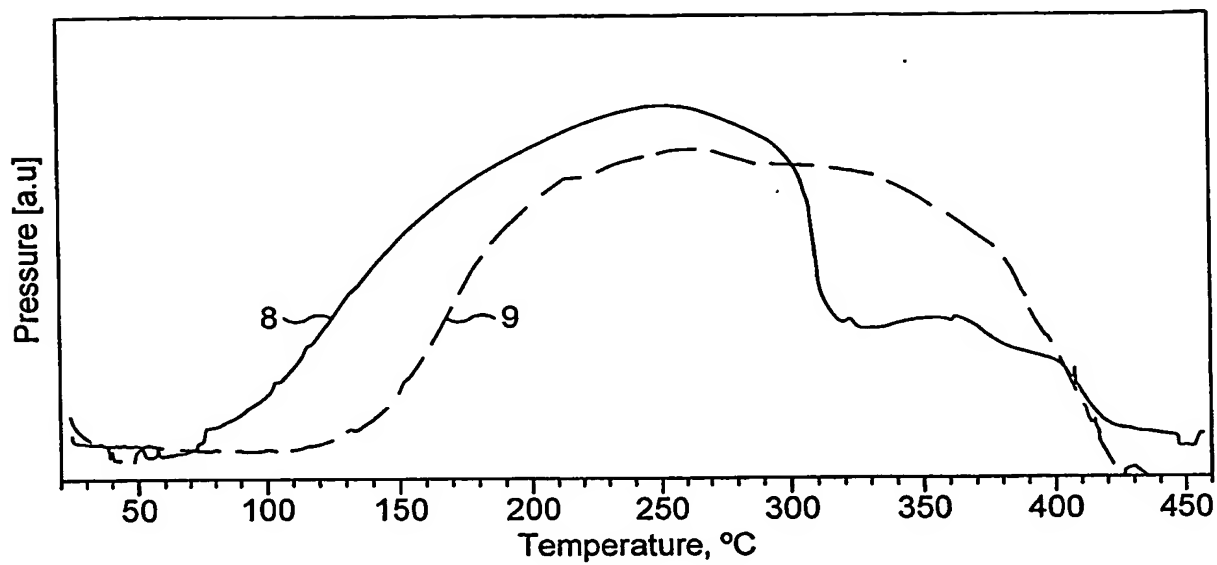


FIG. 3

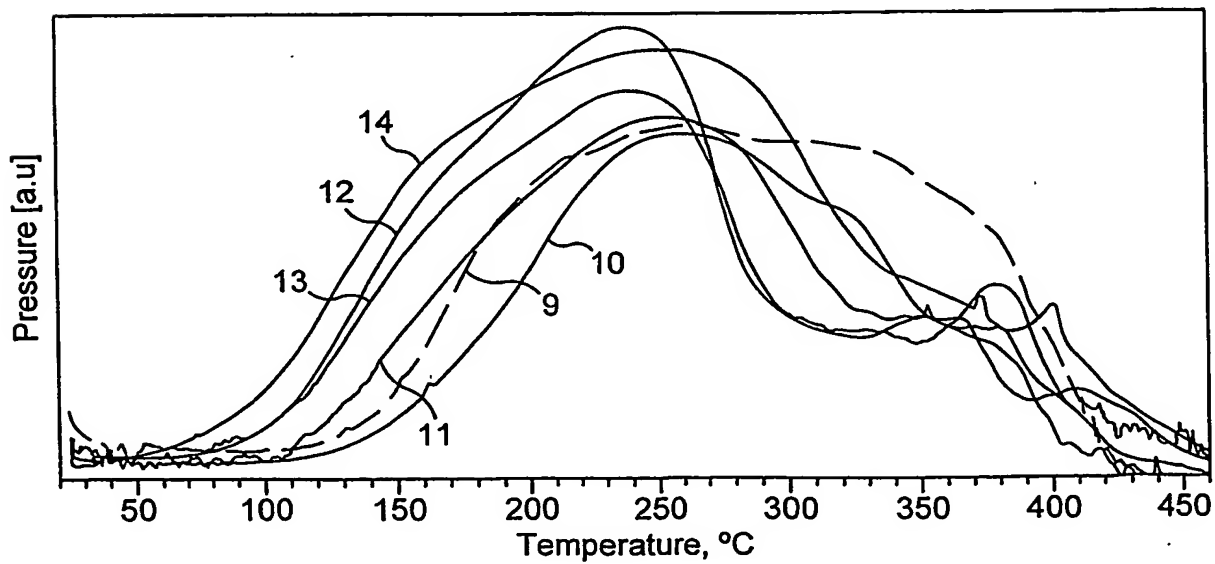


FIG. 4

INTERNATIONAL SEARCH REPORT

• Inter • Application No.
PC 1 / GB 03/03318

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22C1/04 B22F9/02 B22F9/04 H01M4/38 C01B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22C B22F H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 23906 A (SCHULZ ROBERT ;UNIV MCGILL (CA); HYDRO QUEBEC (CA); ZALUSKA ALICJA) 8 August 1996 (1996-08-08) claims 9,10; examples 1,2	1-9
X	claims 1-3 --- -/-	10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

6 October 2003

Date of mailing of the international search report

15/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

González-Junquera, J

INTERNATIONAL SEARCH REPORT

Intern Application No. ...
PCT/GB 03/03318

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZALUSKI L ET AL: "HYDROGEN ABSORPTION IN NANOCRYSTALLINE MG ₂ Ni FORMED BY MECHANICAL ALLOYING" JOURNAL OF ALLOYS AND COMPOUNDS, ELSEVIER SEQUOIA, LAUSANNE, CH, 1 February 1995 (1995-02-01), pages 245-249, XP000570377 ISSN: 0925-8388 page 245, right-hand column, line 6 - last line page 248, right-hand column, last paragraph -page 249, left-hand column, line 11	1-9
X	right-hand column	10
A	US 6 165 643 A (DOYLE MARK LAURENCE ET AL) 26 December 2000 (2000-12-26) claims 1,9,15	1-10
A	VON ZEPPELIN F ET AL: "Hydrogen desorption kinetics of nanostructured MgH ₂ composite materials" JOURNAL OF ALLOYS AND COMPOUNDS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 330-332, 17 January 2002 (2002-01-17), pages 723-726, XP004313364 ISSN: 0925-8388 page 723, right-hand column, last paragraph -page 724, left-hand column, line 15	1-10

INTERNATIONAL SEARCH REPORT

nation on patent family members

Intern:

Application No.:

PCT/GB 03/03318

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9623906	A	08-08-1996	CA 2209777 A1	08-08-1996
			WO 9623906 A1	08-08-1996
			DE 69612972 D1	28-06-2001
			DE 69612972 T2	04-04-2002
			EP 0815273 A1	07-01-1998
			JP 11503489 T	26-03-1999
			US 5964965 A	12-10-1999
US 6165643	A	26-12-2000	AT 220822 T	15-08-2002
			AU 7223598 A	27-11-1998
			CN 1261466 T	26-07-2000
			DE 69806591 D1	22-08-2002
			DE 69806591 T2	27-03-2003
			EP 0979532 A1	16-02-2000
			ES 2181209 T3	16-02-2003
			WO 9850968 A1	12-11-1998
			JP 2002514347 T	14-05-2002
			NO 995292 A	20-12-1999